

Dependence of the Optical Anisotropy of ZnO Thin Films on the Structural Properties

Man-Il KANG and Sok Won KIM

Department of Physics, University of Ulsan, Ulsan 680-749

Yong-Gi KIM and Ji-Wook RYU*

Department of Physics, Kongju National University, Kongju 314-701

(Received 24 February 2010, in final form 21 May 2010)

The structural properties and optical anisotropy of strained ZnO films prepared by rf magnetron sputtering were investigated. Anisotropic complex refractive index spectra of the films were determined by using the Adachi-New Forouhi dispersion model with phase-modulated spectroscopic ellipsometry in the range of 1.0 ~ 4.0 eV. A negative strain was induced by the mismatch between the ZnO film and the Al₂O₃ substrate and decreased with improving crystallinity of the film. The size of the grains formed in the films showed a linear dependence on the strain. The optical anisotropy of the ZnO films was enhanced with improving crystallinity of the films. A shifting of the critical points of the anisotropic complex refractive index spectra was observed due to variations in the strain. The anisotropic complex refractive index spectra showed a strong dependence on structural changes in the ZnO films.

PACS numbers: 78.20.-e, 78.20.Ci, 81.40.Tv, 81.40.-z

Keywords: ZnO, Optical anisotropy, Spectroscopic ellipsometry

DOI: 10.3938/jkps.57.389

I. INTRODUCTION

Zinc oxide (ZnO) is one of the metal-oxide semiconductors suitable for use in optoelectronic devices. ZnO is an *n*-type wide direct-gap semiconductor (3.37 eV) [1]. It has been used extensively as a photo-conducting and fluorescent material, being effective in the visible to ultraviolet spectral region. Also, it can be used with solar cell windows, gas sensors, surface acoustic wave devices and integrated acousto-optic devices [2–4], because ZnO films have excellent optical, piezoelectric and acousto-optic properties [5,6].

Recently, much work has been focused on the epitaxy of ZnO films on (0001) Al₂O₃ [7,8], although the in-plane lattice constant of the films is largely mismatched with that of the (0001) Al₂O₃ substrate. Due to the large mismatch in the lattice constant and the coefficient of thermal expansion between the film and the substrate, biaxial strain is expected to be induced in the films during the growth process. Thus, the band structure of ZnO will be changed with the strain and subsequently modify the optical characteristics, such as the optical constants and the absorption coefficient. Therefore, a study to determine more accurately the effects of strain on the

optical properties of ZnO is needed.

ZnO with a wurtzite crystal structure is optically uniaxial, defined by a dielectric function for light polarized parallel to the *c* axis ($E \parallel c$ or extraordinary, n_e) and by a dielectric function for light polarized perpendicular to the *c* axis ($E \perp c$ or ordinary, n_o) [9]. Thus, the material is optically anisotropic. The optical anisotropy of the bulk ZnO crystal has been studied using several experimental techniques. A high-accuracy minimal deviation method was employed by Bond [10] in the transparent spectral region. Far-ultraviolet reflectance spectra were measured by Freeouf [11] in the photon energy range from 0.6 to 26 eV. Spectroscopic ellipsometry (SE) measurements of optical constants for both $E \parallel c$ and $E \perp c$ of ZnO crystals were performed by Yoshikawa and Adachi [12] and by Jellison and Boatner [9] in the spectral range from 1.5 to 5.0 eV. SE is a nondestructive technique to measure the optical response of a semiconductor. SE extracts both the real and the imaginary parts of the dielectric function directly on a wavelength-by-wavelength basis. In addition, the film thickness can be determined by precise fitting the ellipsometric data with an appropriate dispersion model [13].

In this work, the structural properties and the optical anisotropy of strained ZnO films prepared by rf magnetron sputtering were investigated. The structures and the optical constants of the films for both $E \parallel c$ and E

*E-mail: jwryu@kongju.ac.kr

Table 1. Deposition conditions of ZnO films.

Substrate	RF Power (W)	O ₂ Ratio (%)	Growth Time (min)
Al ₂ O ₃ (0001)	100	0	45
			200
		10	288
			450
		15	200

$\perp c$ were determined by using the Adachi-New Forouhi (ANF) dispersion formula with SE [12]. Also, optical anisotropy change induced by alteration of the crystal structure was analyzed.

II. EXPERIMENTS

1. Preparation of Samples and Measurement of the Structural Properties

ZnO thin films were deposited on (0001) Al₂O₃ substrates by rf magnetron sputtering with a ZnO (99.99%) disk target with a diameter of 4 inch. Sputtering was performed at as rf power of 100 W for various growth times at room temperature, and the distance between the target and the substrate was kept as 10 cm. Ar and O₂ with 99.999% purity were used as sputtering and reactive gases, respectively, with O₂ partial pressures of 0%, 10%, and 15% and a total flow rate of 30 sccm. The base pressure of the chamber was less than 5.0×10^{-6} Torr, and the working pressure of the chamber during the sputtering was about 1.5×10^{-2} Torr at O₂ partial pressure of 0% and about 3.5×10^{-2} Torr at O₂ partial pressures of 10% and 15%. The deposition conditions of ZnO films are shown in Table 1.

The microstructures of ZnO films were investigated using scanning electron microscopy (SEM; Rigaku, D/MAX-Rc), and the crystalline structures of the films were examined using X-ray diffraction (XRD; JEOL, JSM6335F) with Cu $K\alpha$ radiation at a wavelength of 1.54 Å.

2. Measurement and Analysis of the Elliptic Constants

The elliptic constants (Ψ and Δ) of ZnO films were measured by using a phase modulated spectroscopic ellipsometer (PMSE; Jobin-Yvon, Uvisel UV/NIR) [13] in the photon energy region from 1.0 to 4.0 eV in intervals of 0.02 eV at room temperature and at an incident angle of 65°. The structures and optical constants for both $E \parallel c$ and $E \perp c$ of the films were determined

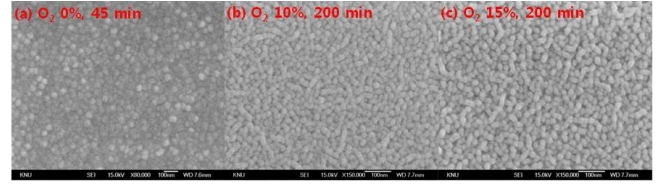


Fig. 1. SEM images of ZnO films deposited on (0001) Al₂O₃ substrate at various O₂ partial pressures.

by fitting the elliptic constants with the ANF dispersion model. The optical structures of the ZnO films for analysis were designed as three layers: an isotropic surface layer, an anisotropic film layer, and an anisotropic Al₂O₃ substrate. The anisotropic optical constants of the Al₂O₃ substrate were taken as values obtained from the DeltaPsi2 program.

From the ANF dispersion model, the complex dielectric function can be expressed as [12]

$$\varepsilon(E) = \varepsilon_0(E) + \varepsilon_1(E) \quad (1)$$

where

$$\varepsilon_0 = A_0 \left\{ \frac{f(X_o)}{E_g^{3/2}} + \frac{f(X_{so})}{2(E_g + \Delta_o)^{3/2}} \right\}, \quad (2a)$$

$$\varepsilon_1(E) = (n_1(E) + ik_1(E))^2, \quad (2b)$$

with

$$n_1(E) = n_\infty + \frac{B(E - \omega_i) + C}{(E - \omega_i)^2 + \Gamma_i^2}, \quad (3a)$$

$$k_1(E) = \begin{cases} \frac{f_j(E - E_g)^2}{(E - \omega_i)^2 + \Gamma_j^2}, & E > E_g \\ 0, & E \leq E_g \end{cases} \quad (3b)$$

n_∞ is the refractive index at high frequency, E_g is the optical band-gap, f_j is the strength of the j th oscillator, ω_j is the resonance angular frequency, and Γ_j is the broadening. Also, Δ_o is the separation of the transition energy by the interaction of the spin-orbit and the crystal fields, Γ_o is the broadening caused by the separation of the transition energy, and A_0 is the probability of the transition.

III. RESULTS AND DISCUSSION

1. Structural Properties

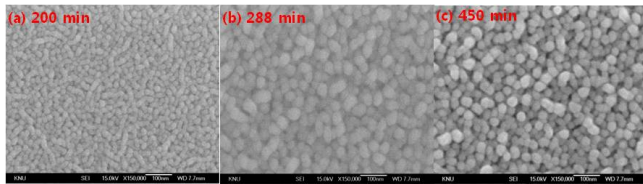
Figure 1 shows SEM images of ZnO films deposited at various O₂ partial pressures on (0001) Al₂O₃ substrates. The surface morphology of the films was found to depend strongly on the O₂ partial pressure. Crystallites in the films were observed, and the surface morphology

Table 2. Structural parameters of ZnO films obtained by analysis of the XRD pattern.

O ₂ Ratio (%)	Growth Time (min)	Peak Angle (degree)	FWHM (degree)	Lattice Constant, <i>C</i> (Å)	Strain (%)	Grain Size (nm)
0	45	34.55	0.292	5.192	-0.269	-
	200	34.72	0.192	5.168	-0.730	18.4
10	288	34.65	0.175	5.178	-0.538	22.7
	450	34.52	0.163	5.196	-0.192	36.0
15	200	34.66	0.196	5.176	-0.576	20.7

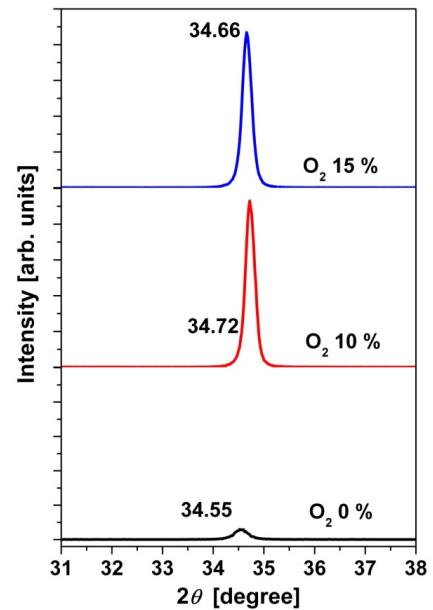
Table 3. Analysis results of ZnO films fitted using the ANF model.

O ₂ Ratio (%)	Growth Time (min)	Surface Layer Void Ratio (%)	Surface Layer Thickness (nm)	ZnO Layer Thickness (nm)	Total Thickness (nm)	χ^2
0	45	70.0	7.2	69.9	77.1	0.515
	200	35.2	24.0	91.9	115.9	0.508
10	288	51.3	25.8	148.1	173.9	1.001
	450	46.6	28.4	221.5	249.9	1.424
15	200	38.7	28.8	86.3	115.1	0.474

Fig. 2. SEM images of ZnO films deposited on (0001) Al₂O₃ substrates for various growth times at a 10% O₂ partial pressure.

was greatly improved with increasing O₂ partial pressure. SEM images of ZnO films deposited on (0001) Al₂O₃ substrates at various growth times at a 10% O₂ partial pressure are shown in Fig. 2. The SEM images show homogeneous ZnO patterns, and the grain size of crystallites formed in the films increased with increasing growth time. The result indicates that the grain size depends on the growth time of the films.

Figure 3 shows the XRD patterns of ZnO films deposited at various O₂ partial pressures on (0001) Al₂O₃ substrates. The XRD patterns at various O₂ partial pressures revealed *c*-axis-oriented ZnO (0002) peaks at $2\theta = 34.55^\circ, 34.72^\circ$. The intensities of the peaks became more intense and sharper with increasing O₂ partial pressure from 0% to 10%, and the positions of the peaks were shifted about 0.18° toward higher diffraction angle. This suggests that the crystallinity of the ZnO films improved greatly with increasing O₂ partial pressure. In the case of increasing O₂ partial pressure from 10% to 15%, the intensities of the peaks decreased slightly, and the positions of the peaks shifted about 0.06° toward lower diffraction angle. Figure 4 shows the XRD patterns of

Fig. 3. XRD pattern of ZnO films deposited on (0001) Al₂O₃ substrates at various O₂ partial pressures.

ZnO films deposited on (0001) Al₂O₃ substrates at various growth times at a 10% O₂ partial pressure. The XRD patterns for various growth times showed *c*-axis-oriented ZnO (0002) peaks at $2\theta = 34.72^\circ, 34.65^\circ, \text{ and } 34.52^\circ$. The intensities of peaks became gradually more intense and sharper with increasing growth time from 200 minutes to 450 minutes, and the positions of the peaks were shifted about 0.07° and 0.20° toward lower diffraction angle. This indicates that the crystallinity of the ZnO

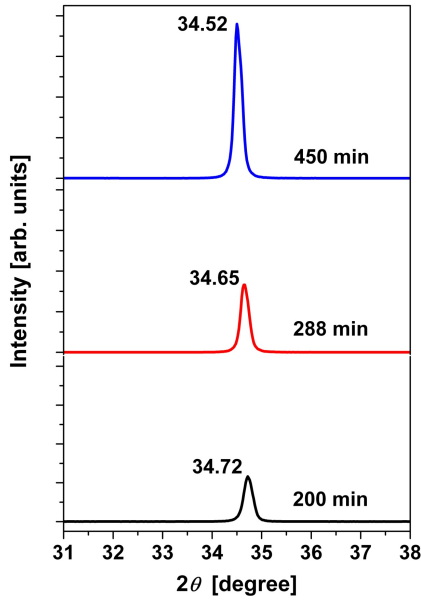


Fig. 4. XRD patterns of ZnO films deposited on (0001) Al_2O_3 substrates for various growth times at a 10% O_2 partial pressure.

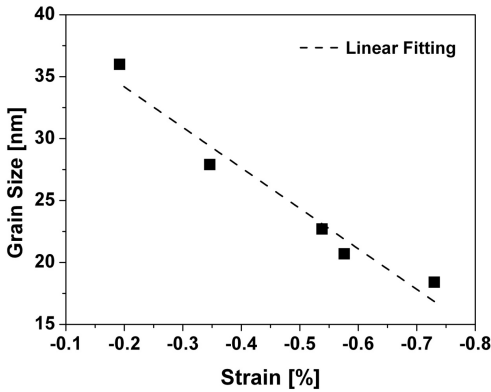


Fig. 5. Dependence of grain size on the c -axis strain, ε_{zz} .

films highly improved with increasing growth time and that the grain size becomes larger.

The c -axis lattice constant of the ZnO films was obtained by doubling the interplanar spacing d of the basal planes, which was calculated from the position of the (0002) peak by using the Bragg condition. Then, the strain along the c -axis of the films was calculated by using the following equation [14]:

$$\varepsilon_{zz} = \frac{c - c_0}{c_0} \times 100\%, \quad (4)$$

where c_0 , with a value of 5.207 Å, is the unstrained lattice constant of ZnO powder [15]. In addition, the mean grain size of the ZnO films, which reflects strain effects, was estimated by using the Scherrer formula [16,17] with the full width at half maximum (FWHM) of the (0002)

peak. The structural parameters of the ZnO films obtained by analysing the XRD patterns are shown in Table 2. According to the results of Table 2, the strains of the ZnO films deposited on (0001) Al_2O_3 substrates at various growth conditions revealed negative values, and the largest value was to -0.730 in the film deposited for 200 minutes at a 10% O_2 partial pressure. The negative strain values represent compressive strain along the c -axis and are induced by the large mismatch between the ZnO film and the (0001) Al_2O_3 substrate in the in-plane lattice constant. The best crystallinity was observed in the film deposited for 450 minutes at a 10% O_2 partial pressure. The c -axis lattice constant of the film, which yields a d spacing of 2.598 Å, is in good agreement with the lattice constant of bulk ZnO ($c = 2d = 5.213$ Å) [18]. The mean grain sizes of the ZnO films were 18.4, 22.7, and 36.0 nm for the films grown for 200, 288, and 450 minutes at a 10% O_2 partial pressure, respectively. This result indicates that the grain size increases with increasing thickness of the film and is in good agreement with the SEM result. Figure 5 shows the grain size as a function of the c -axis strain. The negative strain was found to be inversely proportional to the grain size. This result implies that the strain is relieved with increasing grain size.

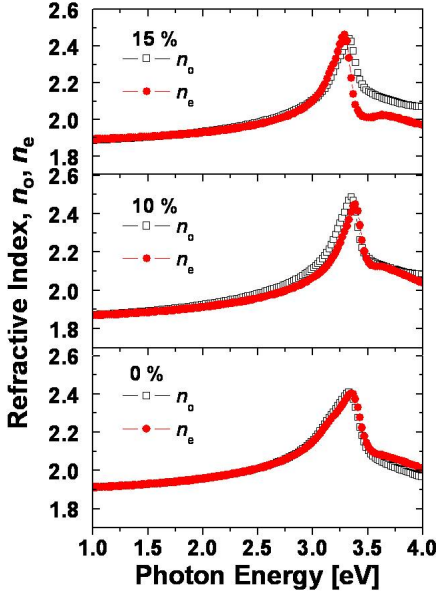
2. Optical Anisotropy

The analysis results of ZnO films fitted using the ANF model are shown in Table 3. According to the results of the Table 3, the thickness of the surface layer increased with improving crystallinity of the ZnO films, and the thickness of the ZnO layer increased with increasing growth time. The thicknesses of the surface and the ZnO layer of the film deposited for 450 minutes at a 10% O_2 partial pressure were found to be 28.4 and 221.5 nm, respectively.

Figure 6 shows anisotropic refractive index (n_o , n_e) spectra of ZnO films deposited on Al_2O_3 substrates at various O_2 partial pressures. Below the band edge (~ 3 eV), the n_o and the n_e spectra of the films became a little smaller with increasing O_2 partial pressure from 0% to 10%. As the O_2 partial pressure increased from 10% to 15%, the n_o and the n_e spectra of the films nearly did not change. From a comparison of the analysis results of the XRD patterns shown in Table 2, the critical points (CPs) of the n_o spectra of the films deposited at various O_2 partial pressures were nearly not shifted with increasing strain. However, the CPs of the n_o spectra were moved toward higher energy with increasing strain. Figure 7 shows anisotropic extinction coefficient (k_o , k_e) spectra of ZnO films deposited on Al_2O_3 substrates at various O_2 partial pressures. The difference between the k_o and the k_e spectra of the films became larger with increasing O_2 partial pressure. The CPs of the k_o spectra were nearly not shifted with increasing strain, but the CPs of

Table 4. Anisotropic refractive indices of ZnO film determined by using the ANF dispersion formula.

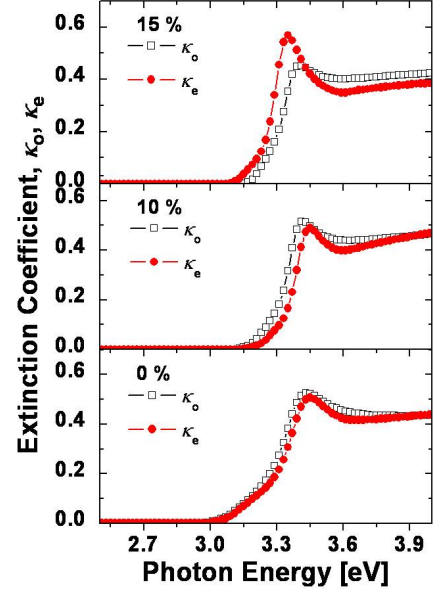
Photon Energy (eV)	1.55		1.77		2.07		2.47		2.75	
Sample	n_o	n_e	n_o	n_e	n_o	n_e	n_o	n_e	n_o	n_e
This study	1.951	1.973	1.963	1.980	1.984	1.992	2.026	2.017	2.075	2.046
Bond	1.959	1.975	1.973	1.989	1.998	2.014	2.051	2.068	2.105	2.123
Jellison	1.961	1.976	1.974	1.990	1.997	2.015	2.047	2.065	2.104	2.121

Fig. 6. Anisotropic refractive index spectra of ZnO films deposited on Al_2O_3 substrates at various O_2 partial pressures.

the k_e spectra were shifted toward higher energy with increasing strain.

Anisotropic refractive index spectra of ZnO films deposited on Al_2O_3 substrates for various growth times at a 10% O_2 partial pressure are shown in Fig. 8. The difference between the n_o and the n_e spectra of the films became larger with improving crystalline quality and optical anisotropy of ZnO films. The CPs of the n_o spectra of the films were shifted toward higher energy with decreasing strain due to the increasing grain size and thickness of the film, but the CPs of the n_e spectra of the films were moved toward lower energy. Figure 9 shows anisotropic extinction coefficient spectra of ZnO films deposited on Al_2O_3 substrates for various growth times at a 10% O_2 partial pressure. The CPs of the k_o spectra were shifted toward higher energy with decreasing strain, but the CPs of k_e the spectra were shifted toward lower energy with decreasing strain. This result indicates that the optical anisotropy of the ZnO films strongly depends on the structural properties, such as crystallinity, grain size, and strain. In particular, anisotropic complex refractive index spectra of ZnO films sensitively responded to variations in the strain in the film.

When the optical constant of the materials is deter-

Fig. 7. Anisotropic extinction coefficient spectra of ZnO films deposited on Al_2O_3 substrates at various O_2 partial pressures.

mined by using spectroscopic ellipsometry, a parameter estimating method using a dispersion formula is generally utilized. In such a case, because a strong correlation between the fitting parameters may be revealed, the validity of the fitting results should be confirmed. In this study, to verify the properness of the fitting results, we compared the anisotropic refractive indices of the film deposited for 450 minutes at a 10% O_2 partial pressure with those obtained by Bond and Jellison in Table 4 [19]. The values of this study were in good agreement with the data. This result implies that the fit by using the ANF dispersion formula is valid.

IV. CONCLUSION

The variations in the optical anisotropy of ZnO thin films with changes in the structural properties under various growth conditions were investigated. The structures and the anisotropic complex refractive index spectra of the films were determined by using the Adachi-New Forouhi dispersion model with phase-modulated spectroscopic ellipsometry in the range of 1.0 ~ 4.0 eV. The

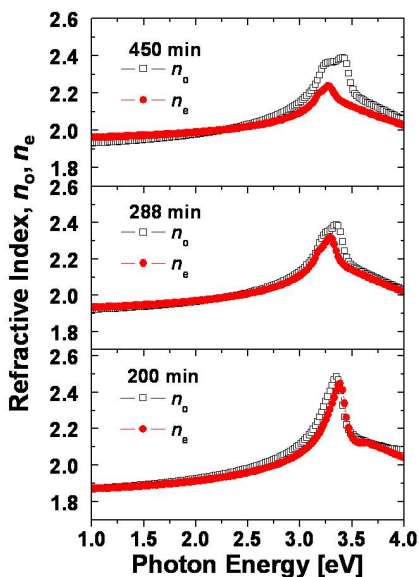


Fig. 8. Anisotropic refractive index spectra of ZnO films deposited on Al₂O₃ substrates for various growth times at a 10% O₂ partial pressure.

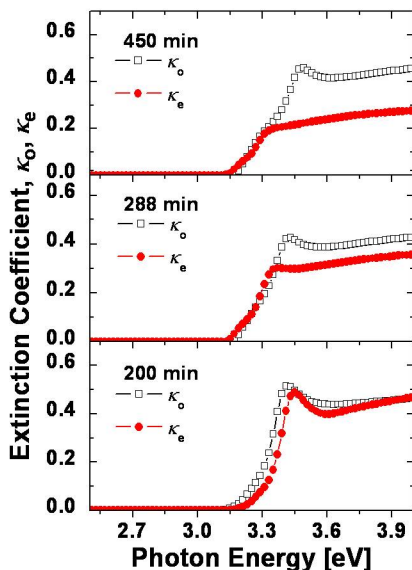


Fig. 9. Anisotropic extinction coefficient spectra of ZnO films deposited on Al₂O₃ substrates for various growth times at a 10% O₂ partial pressure.

optical anisotropy change induced by variations in the crystal structure was also determined.

A negative strain was induced due to the mismatch between the ZnO film and the Al₂O₃ substrate and decreased with improving crystallinity of the film. The sizes of the grains formed in the films showed a linear dependence on the strain. The optical anisotropy of

the ZnO films was enhanced with improving crystallinity of the films. Also, a shifting of the critical points of the anisotropic complex refractive index spectra was observed due to variations in the strain. The anisotropic complex refractive index spectra showed a strong dependence on structural changes in the ZnO films.

ACKNOWLEDGMENTS

This work was supported by the Priority Research Centers Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2009-0093818).

REFERENCES

- [1] A. Ohtomo, M. Kawasaki, I. Ohkubo, H. Koinuma, T. Yasuda and Y. Segawa, *Appl. Phys. Lett.* **75**, 980 (1999).
- [2] D. M. Bagnall, Y. F. Chen, Z. Zhu, T. Yao, M. Y. Shen and T. Goto, *J. Crystal Growth* **184-185**, 605 (1998).
- [3] C. H. Ahn, Y. Y. Kim, S. W. Kang and H. K. Cho, *Physica B* **401-402**, 370 (2007).
- [4] H. S. Kang, G. H. Kim, H. W. Chang, B. D. Ahn and S. Y. Lee, *Appl. Phys. Lett.* **89**, 181103 (2006).
- [5] Y. J. Lin, C. L. Tsai, Y. M. Lu and C. J. Liu, *J. Appl. Phys.* **99**, 093501 (2006).
- [6] S. J. Pearton, D. P. Norton, K. Ip and Y. W. Heo, *J. Vac. Sci. Technol., B* **22**, 932 (2004).
- [7] D. K. Hwang, H. S. Kim, J. H. Lim, J. Y. Oh, J. H. Yang and S. J. Park, *Appl. Phys. Lett.* **86**, 151917 (2005).
- [8] G. Hu, H. Gong, E. F. Chor and P. Wu, *Appl. Phys. Lett.* **89**, 251102 (2006).
- [9] G. E. Jellison, Jr. and L. A. Boatner, *Phys. Rev.* **58**, 3586 (1998).
- [10] W. L. Bond, *J. Appl. Phys.* **36**, 1674 (1965).
- [11] J. L. Freeouf, *Phys. Rev. B* **7**, 3810 (1973).
- [12] H. Yoshikawa and S. Adachi, *Jpn. J. Appl. Phys., Part 1* **36**, 6237 (1997).
- [13] H. Fujiwara, *Spectroscopic Ellipsometry* (Wiley, Tokyo, 2007).
- [14] H. C. Ong, A. X. E. Zhu and G. T. Du, *Appl. Phys. Lett.* **80**, 941 (2002).
- [15] M. K. Puchert, P. Y. Timbrell and R. N. Lamb, *J. Vac. Sci. Technol., A* **14**, 2220 (1996).
- [16] B. D. Cullity, *Elements of X-Ray Diffractions* (Addison-Wesley, Reading, MA, 1978).
- [17] R. W. Vook, in *Epitaxial Growth*, edited by J. W. Matthews (Academic, New York, 1975).
- [18] Y. Chen, D. M. Bagnall, H. J. Koh, K. T. Park, K. Hiraga, Z. Zhu and T. Yao, *J. Appl. Phys.* **84**, 3912 (1998).
- [19] G. E. Jellison, Jr. and F. A. Modin, *Appl. Phys. Lett.* **69**, 371 (1996).